

Mid-Pliocene sea level and continental ice volume based on coupled benthic Mg/Ca palaeotemperatures and oxygen isotopes

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Ostracode magnesium/calcium (Mg/Ca)-based bottom-water temperatures were combined with benthic foraminiferal oxygen isotopes in order to quantify the oxygen isotopic composition of seawater, and estimate continental ice volume and sea-level variability during the Mid-Pliocene warm period, ca 3.3–3.0 Ma. Results indicate that, following a low stand of approximately 65 m below present at marine isotope stage (MIS) M2 (ca 3.3 Ma), sea level generally fluctuated by 20–30 m above and below a mean value similar to present-day sea level. In addition to the low-stand event at MIS M2, significant low stands occurred at MIS KM2 (-40 m), G22 (-40 m) and G16 (-60 m). Six high stands of +10 m or more above present day were also observed; four events (+10, +25, +15 and +30 m) from MIS M1 to KM3, a high stand of +15 m at MIS K1, and a high stand of +25 m at MIS G17. These results indicate that continental ice volume varied significantly during the Mid-Pliocene warm period and that at times there were considerable reductions of Antarctic ice.

Keywords: Pliocene; sea level; ice volume; Mg/Ca; global warming

1. Introduction

One potential impact of global warming is the inundation of the Earth's low-lying coastal areas by rising sea level caused by the melting of alpine glaciers and small ice caps and portions of the Greenland and Antarctic ice sheets (AIS). Historical observations from tidal gauges and more recent satellite records provide a short-term perspective on rates of sea-level rise, but these may not be relevant under a possible new equilibrium climate state associated with elevated greenhouse gas concentrations. Climate model simulations provide some constraints on future rates and estimates of ultimate amplitudes under expected conditions of continued global warming, but are unable to forecast rapid non-linear changes in ice sheet stability caused by a variety of processes under the umbrella of 'ice dynamics' (e.g. Truffer & Fahnestock 2007).

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To better understand the sea level and continental ice sheet stability during periods of climatic warmth, we reconstructed ice volume and sea level for the Mid-Pliocene warm period (ca 3.3-3.0 Ma), a period proposed as a possible model for future climate (Dowsett et al. 1996). Numerous previous studies have examined the topic of continental ice volume and sea-level change during the Mid-Pliocene warm period (e.g. Dowsett & Cronin 1990; Webb & Harwood 1993; Kennett & Hodell 1995; Warnke et al. 1996; Naish et al. 2005; see Hill et al. 2007 for a review) with considerable focus on the question of the stability of the AIS. No clear consensus has emerged, although reasonable arguments have been presented for both stable and unstable Antarctic ice during the Pliocene. Briefly, estimates of maximum sea-level elevations during the Mid-Pliocene range from 10 to 35 m above present. perhaps higher, which would have inundated many low-lying coastal regions. Assuming minimal Northern Hemisphere continental ice volume prior to ca3 Ma, such high stands of sea level suggest a significant reduction of Antarctic continental ice volume. Most estimates for Pliocene sea level are based on the elevations of palaeoshorelines and shallow marine sediments corrected for uplift (e.g. Dowsett & Cronin 1990) and continental margin sequence stratigraphy combined with benthic marine δ^{18} O records (Miller *et al.* 2005). A number of indirect approaches, most using deep-sea δ^{18} O records. also have been used to estimate ice volume (Labervie et al. 1987; Schrag et al. 1996). Neither coastal stratigraphy and geomorphology nor deep-sea isotopic records have yet provided definitive sea-level and ice-volume estimates for the Mid-Pliocene.

In this study we combine ostracode Mg/Ca-based deep ocean temperatures and benthic for aminiferal δ^{18} O data from the same samples to produce quantitative records of the δ^{18} O of Mid-Pliocene seawater. The advantage of the coupled Mg/Ca- δ^{18} O approach, which has been applied to the Late Pliocene (Dwyer *et al.* 1995) and Late Quaternary climate cycles (Dwyer *et al.* 1995; Lea *et al.* 2002), is that it allows for a continuous, independent assessment of continental ice volume and sea-level history during the Mid-Pliocene.

2. Methodology

The $\delta^{18}{\rm O}$ of benthic for aminifera is mainly controlled by water temperature and by continental ice volume. The latter influences $\delta^{18}{\rm O}$ of seawater ($\delta^{18}{\rm O}_{\rm sw}$) through the well-known process of evaporation and transfer of $^{16}{\rm O}$ -enriched waters from the ocean into the continental ice sheets during glacial intervals and subsequent release of those relatively 'lighter' waters back to the ocean upon ice sheet melting during interglacial periods. With oceanic mixing times of approximately 1000 years, the ice volume $\delta^{18}{\rm O}$ signal transmits rapidly through the global ocean as demonstrated by the successful use of $\delta^{18}{\rm O}_{\rm foram}$ as a fundamental tool for chronostratigraphic correlation. However, as a function of both the oxygen isotopic composition and the temperature of ambient seawater, benthic $\delta^{18}{\rm O}_{\rm foram}$ records have confounded investigators hoping to reconstruct these two important palaeoclimate parameters. With only the $\delta^{18}{\rm O}_{\rm foram}$, neither the $\delta^{18}{\rm O}_{\rm sw}$ nor the palaeotemperature can be reliably determined without independent quantification of one or the other.

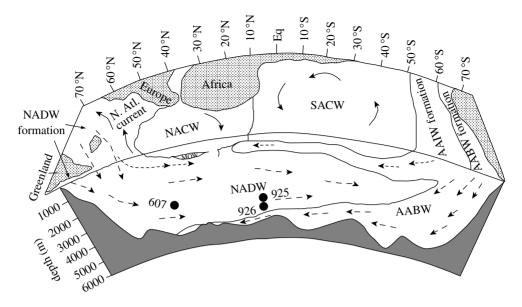


Figure 1. Schematic of Atlantic Ocean showing location of study sites in relation to circulation patterns and water masses (after Pickard & Emery 1982; Dwyer et al. 2002). Water masses: NADW, North Atlantic deep water; MOW, Mediterranean outflow water; AABW, Antarctic bottom water; AAIW, Antarctic intermediate water; NACW, North Atlantic central water; SACW, South Atlantic central water. General current directions are indicated by arrows: deep waters (long dashes), intermediate waters (short dashes) and surface waters (solid).

We use paired samples of Mg/Ca-based bottom-water temperature (BWT) from ostracodes and the $\delta^{18}O_{\rm foram}$ to solve for $\delta^{18}O_{\rm sw}$, as follows: $\delta^{18}O_{\rm cal(PDB)} = \delta^{18}O_{\rm sw}$ (SMOW) + (2.78)(10^6)(T^{-2}) – 33.3557, where PDB is Pee Dee Belemnite; $\delta^{18}O_{\rm cal}$ is the oxygen isotopic composition of calcite in per mil (in this case, benthic foraminifer shells); T is water temperature in kelvin; SMOW is standard mean ocean water; and $\delta^{18}O_{\rm sw}$ is the oxygen isotopic composition of seawater in per mil (from McCorkle et~al.~1990, modified from O'Neil et~al.~1969). Once the $\delta^{18}O_{\rm sw}$ is determined, it can be used to estimate palaeo-sea level with the assumption that any changes in $\delta^{18}O_{\rm sw}$ result primarily from changes in global continental ice volume (Mix & Pisias 1988), and furthermore that a shift in $\delta^{18}O_{\rm sw}$ of 0.1 per mil is equivalent to a 10 m shift in eustatic sea level (Shackleton & Opdyke 1973).

The primary site selected for this study is Deep Sea Drilling Program (DSDP) Site 607 (figure 1) in the North Atlantic Ocean (41° N, 33° W). At 3427 m water depth, Site 607 is located in the modern-day core of North Atlantic deep water (NADW), with a modern BWT of 2.6°C and modern $\delta^{18}O_{sw}$ of +0.1 per mil (Craig & Gordon 1965). During periods of global cooling, the influence of NADW is diminished at this site (e.g. Boyle & Keigwin 1985) relative to deep water derived from the southern ocean (AABW) which presently has BWT of approximately 0°C and $\delta^{18}O_{sw}$ of approximately -0.5 per mil (Craig & Gordon 1965). Approximately 110 samples were collected from the Mid-Pliocene of Site 607 at an average interval spacing of 17 cm, providing a temporal resolution of ca 4 kyr through the Mid-Pliocene warm period. Large-volume samples (approx. 30 cm³) were collected and processed to ensure ample material for both ostracode Mg/Ca ratio and benthic foraminiferal oxygen isotopic analyses.

For ostracode Mg/Ca–BWT determinations, sediments were processed and shells were cleaned and analysed for Mg/Ca ratios following procedures described previously (e.g. Dwyer et al. 1995, 2000, 2002; Cronin et al. 1999, 2005). For this study, six adult shells of the ostracode genus Krithe were picked, cleaned and analysed individually from each of the 110 intervals sampled. The averages of these six Mg/Ca measurements are reported here and were used to calculate BWT for each interval using the Krithe core-top Mg/Ca–BWT calibration from Dwyer et al. (1995, 2002). The use of intrasample averages reduces the prediction error to approximately 0.5°C for each BWT calculation (Dwyer et al. 1995). This calibration error is equivalent to approximately twice the analytical error of the Mg/Ca ratio analysis.

For benthic foraminiferal δ^{18} O analyses, an average of three specimens of *Cibicidoides wuellerstorfi* were picked from the greater than 250 µm sediment fraction from each interval and analysed as a bulk sample for oxygen isotopic composition on a MAT 251 IRMS equipped with a Kiel device in the Stable Isotope Laboratory at North Carolina State University under the direction of William J. Showers. Standard reproducibility was approximately 0.06 per mil for δ^{18} O analyses.

Chronology for the Site 607 records presented here is based on correlating the benthic δ^{18} O record generated in this study with the global benthic δ^{18} O stack constructed by Lisiecki & Raymo (2005). Site 607 was selected as the primary focus for this study for a number of reasons. Its location on the mid-Atlantic Ridge is a classic site for Neogene palaeoceanographic reconstructions owing to its sensitivity to deep ocean circulation changes (e.g. Ku et al. 1972; Boyle & Keigwin 1985; Lea & Boyle 1989; Raymo et al. 1989). Site 607 is located in the core of NADW near the upstream sector of the ocean's thermohaline circulation system; it should thus serve as both an integrator of and a rapid responder to glacial-integrational changes in oceanic $\delta^{18}O_{\text{sw}}$. Moreover, our work on the last two glacial-interglacial cycles and the Late Pliocene at this site (Dwyer et al. 1995) provides an important baseline for the additional Mg/Ca study of the Mid-Pliocene warm period. Furthermore, earlier studies (Dwyer et al. 1995; Cronin et al. 1999) have demonstrated a relatively high abundance of well-preserved shells of ostracode genus Krithe at this site. Through the Mid-Pliocene interval, for example, shells show an average VPI (visual preservation index; Dwyer et al. 1995) of 3.4 ± 0.3 (1 s.d.), where 1 is pristine, glassy, clear and unaltered and 7 is highly dissolved/corroded opaque white.

One potential factor in the interpretation of Site 607 is the impact of changes in the relative strength of northern and southern source deep water on the benthic δ^{18} O system at the site. Today, and presumably during the Mid-Pliocene, southern source deep waters have (had) considerably lighter $\delta^{18}O_{sw}$ relative to northern source deep waters due to their different processes of formation (Craig & Gordon 1965). At times when southern source waters dominate the site, such as during glacial periods (e.g. Boyle & Keigwin 1985), benthic δ^{18} O would be biased towards lighter values. Likewise, during interglacial periods, when northern source waters typically dominate at the site, benthic δ^{18} O would be biased towards heavier values. To account for this bias, we apply a water-mass normalization factor to the $\delta^{18}O_{sw}$ values, which is calculated using the Mg/Cabased BWT and a simple linear equation derived from the modern temperature and δ¹⁸O_{sw} values for the Atlantic Ocean deep waters (listed above in Site 607 hydrographic description). Dwyer et al. (1995) did not apply such a water-mass normalization, which may have led to some of the over- and underestimating calculated $\delta^{18}O_{\text{sw}}$ and sea-level values in that study.

An alternative means of normalizing for water-mass differences in $\delta^{18}O_{sw}$ might be to use benthic for aminiferal carbon isotopic composition or Cd/Ca ratios, which have been used as proxies for water mass based on nutrient content/extent of remineralization of organic carbon (Curry & Lohman 1983; Boyle & Keigwin 1985). However, given that water-mass changes at the site are probably density driven, and that the $\delta^{18}O_{sw}$ variability is probably linked to changes in salinity, which in turn combine with temperature changes to form density changes, it is arguably more reasonable to use a conservative water-mass property such as BWT as a means to normalize for possible impacts of changes in water-mass proportions on $\delta^{18}O_{sw}$ at the site. The general covariance of ostracode Mg/Ca and benthic for aminiferal Cd/Ca and δ^{13} C in the deep North Atlantic (e.g. Dwyer *et al.* 1995) further justifies the BWT-based $\delta^{18}O_{sw}$ normalization. Finally, during the Late Pliocene, benthic δ^{13} C has been shown to be out-of-phase relative to $\delta^{18}O$ and Mg/Ca (Dwyer *et al.* 1995); thus, a δ^{13} C-based water-mass normalization might alias the result.

Estimating the error of this approach is difficult in that the $\delta^{18}O_{sw}$ –BWT relationship, which is controlled by sea-surface E/P ratios, shifts in the location or production rates of northern and southern source deep waters, and potentially other processes, is not known for the Mid-Pliocene. The pattern of ocean thermohaline circulation during the Mid-Pliocene was generally similar to the modern (Raymo *et al.* 1996), leading us to conclude that a similar $\delta^{18}O_{sw}$ –BWT relationship may have been present in the deep waters of the Atlantic Ocean at this time.

Ideally, these two proxies would be derived from the same shell material. In addition to analytical error, an additional source of error may be introduced by coupling $\delta^{18}O$ and Mg/Ca from foraminifers and ostracodes, respectively. This approach is nonetheless justified because benthic Mg/Ca–BWT calibrations are best known for ostracodes, whereas benthic $\delta^{18}O$ calibrations are best known for foraminifers. Furthermore, recent work by Elderfield *et al.* (2006) indicates the potential for a strong influence of calcite saturation state of ambient waters as a primary control on Mg/Ca ratios in benthic foraminiferal shells. While additional research is needed, initial results suggest that calcite saturation state has minimal impact on ostracode Mg/Ca ratios (Dwyer *et al.* 1995, 2000, 2002), especially at a site such as 607 where CaCO₃ preservation implies well-saturated waters during the Mid-Pliocene.

We used two strategies to test the validity of the coupled $\delta^{18}O_{foram}$ –Mg/Ca–BWT approach. First, we applied the technique at relatively low temporal resolution to two additional sites in the Atlantic, Ocean Drilling Program Sites 925 and 926 (figure 1), to determine if a similar range of $\delta^{18}O_{sw}$ and sea levels would be obtained at different sites. Sites 925 and 926 (both at approx. 4° N, 43° W) also are presently situated in NADW, south of and downstream from Site 607, at water depths of 3041 and 3598 m, with modern BWTs of 2.7 and 2.4°C, respectively. Chronology for Sites 925 and 926 is based on Tiedemann & Franz (1997 and references therein). Sample processing and analysis of ostracode Mg/Ca ratios and $\delta^{18}O_{foram}$ followed the same procedures used for Site 607.

The second test was to apply the coupled $\delta^{18}O_{foram}$ –Mg/Ca–BWT approach (with water-mass normalization) to previously published data (Dwyer *et al.* 1995) for the last two glacial–interglacial cycles from the *Chain* 82-24

piston-core record (42° N, 33° W) collected nearby Site 607. This allows us to evaluate the technique for a period when the magnitude of ice-volume and sealevel fluctuations is fairly well known.

3. Results and discussion

The results from Site 607 are shown in figure 2a-c. Benthic δ^{18} O (figure 2a) values range from 3.1 to 4.1 per mil and display most of the prominent marine isotope stages (MISs) for this interval. The Mid-Pliocene benthic δ^{18} O range is approximately half that observed for the Late Quaternary, with the lightest Mid-Pliocene values just slightly lower than the value of approximately 3.2 per mil obtained at this site for MIS 5e and the Holocene (figure 2a).

Site 607 ostracode Mg/Ca ratios range from 8.6 to $10.8 \text{ mmol mol}^{-1}$ and show a pattern of variability similar to the $\delta^{18}\mathrm{O}_{\mathrm{foram}}$ record (figure 2b). Converted to BWT, the Mg/Ca ratios indicate temperature fluctuations of approximately 1–1.5°C around a mean BWT value of 2.69°C, which is close to the modern-day BWT of 2.6°C at this site. There is considerable variability in the Mg/Ca–BWT record, which appears to be at or near precessional frequencies. In addition, there is a maximum shift during the Mid-Pliocene of approximately 2°C. This amount is roughly two-thirds of the magnitude of the BWT oscillations during the Late Pliocene 41 kyr climate cycles (Dwyer *et al.* 1995), and half of the magnitude of those during 100 kyr glacial–interglacial cycles of MIS 7-1 (Dwyer *et al.* 1995; Cronin *et al.* 1999). These patterns suggest an interrelationship between the amplitude of orbital climate variability and that of deep ocean temperature and presumably ocean circulation.

The results of the coupled Mg/Ca–BWT and benthic δ^{18} O analysis for Site 607 are shown in figure 2c. The calculated δ^{18} O_{sw} values range from -0.2 to +0.8, which equates to a maximum sea-level change of approximately 100 m. Sea level would have oscillated from approximately 30 m above modern to approximately 70 m below present-day sea level. The heaviest δ^{18} O_{sw} values occur at MIS M2 and G16, and correspond to extreme sea-level low stands of -70 and -60 m, respectively. Three other δ^{18} O_{sw} maxima and sea-level low stands of approximately -40 m occurred during KM2, G20 and around KM6. Aside from these five major low stands, the data indicate that sea level rarely dropped below -25 m during the Mid-Pliocene warm period. In addition to low stands, there were a number of high stands of sea level that reached well above present-day sea level. The lightest δ^{18} O_{sw} values, and associated high stands of sea level, occurred near KM5, at KM3 and at G16 and indicate that sea level at these times reached elevations of +25 to +30 m. Additional δ^{18} O_{sw} minima lie between M1 and KM3 and at K1, indicating at least three other significant sea-level high stands, with elevations of the order of +10 to +20 m.

The accuracy of this approach relies on a number of considerations not the least of which is the reliability of the ostracode Mg/Ca palaeotemperature proxy. Factors other than temperature might affect the Mg/Ca ratios. For example, dissolution (Rosenthal et al. 2000) and carbonate ion saturation (Elderfield et al. 2006) can significantly affect Mg/Ca ratios of benthic and planktonic foraminifera, respectively. While the impact of dissolution and carbonate ion saturation on Krithe Mg/Ca ratios appears to be negligible (Dwyer et al. 1995, 2000, 2002),

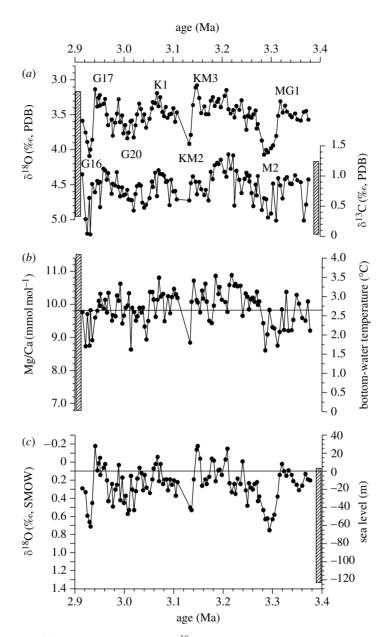


Figure 2. Site 607. (a) Benthic for aminiferal δ^{18} O. Box along the left represents a range of values measured at this site for the Late Quaternary climate cycles. (b) Ostracode Mg/Ca ratios and Mg/Ca-based BWT. Horizontal line represents modern BWT at Site 607. (c) Calculated and normalized δ^{18} O of seawater and calculated sea level (see text for explanation of calculations). Box at the right represents a range of values calculated for the Late Quaternary climate cycles in reanalysis of nearby *Chain* core 82-24-4PC using the same approach applied in this study.

especially at a North Atlantic location such as Site 607, it is difficult to conclusively assess the possible impact of these factors in down-core data. Therefore, in an attempt to test the validity of the results from Site 607, we

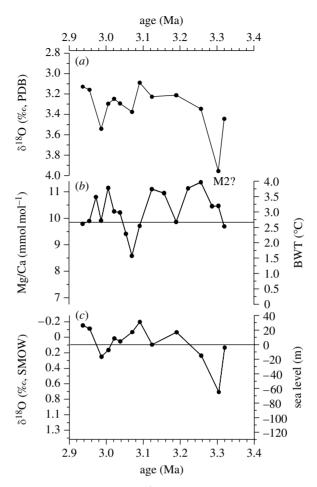


Figure 3. Site 925. (a) Benthic for aminiferal δ^{18} O. (b) Ostracode Mg/Ca ratios and Mg/Ca-based BWT. Horizontal line represents modern BWT at Site 925. (c) Calculated and normalized δ^{18} O of seawater at Site 925 and calculated sea level (see text for explanation of calculations).

applied the coupled Mg/Ca–BWT–benthic δ^{18} O approach to previously published Mg/Ca data from MIS 7-1 (Dywer et al. 1995) incorporating the water-mass normalization factor discussed above. The results are summarized in figure 2c in the form of a box covering the range of δ^{18} O_{sw} and sea-level values obtained with the water-mass normalization. This new calculation yields a sea-level range of approximately 126 m with low stand of approximately -121 m and high stand of approximately +5 m. This range and the absolute values are identical to the consensus sea-level values of the last glacial maximum and the last interglacial MIS 5e (Thompson & Goldstein 2005; Peltier & Fairbanks 2006 and references therein), supporting the validity of the coupled Mg/Ca–BWT–benthic δ^{18} O approach. As expected, the primary impact of the water-mass normalization is to reduce the amplitude of the un-normalized result.

To further evaluate the Mid-Pliocene sea-level estimates from Site 607, we tested the method on two additional ODP Sites (925 and 926) from the Ceara Rise in the equatorial western North Atlantic (figures 3a-c and 4a-c). While the

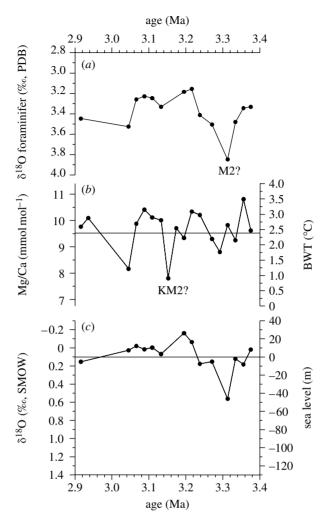


Figure 4. Site 926. (a) Benthic for aminiferal δ^{18} O. (b) Ostracode Mg/Ca ratios and Mg/Ca-based BWT. Horizontal line represents modern BWT at Site 926. (c) Calculated and normalized δ^{18} O of seawater at Site 926 and calculated sea level (see text for explanation of calculations).

data are of lower resolution than Site 607 and do not allow for direct correlation, the calculated Mid-Pliocene $\delta^{18}O_{sw}$ values and the resultant sea levels for Sites 925 and 926 nevertheless display a general pattern of variability that is similar to that observed at Site 607. Furthermore, the overall magnitude, approximate timing and absolute values of the changes in $\delta^{18}O_{sw}$ and sea level at Sites 925 and 926 are consistent with the record calculated from Site 607, including the major sea-level low-stand event at MIS M2 and sea-level high stands reaching up to a maximum of approximately +30 m (figures 3c and 4c).

These tests of validity support the hypothesis that the coupled ostracode Mg/Ca–BWT–benthic foram $\delta^{18}{\rm O}$ approach can be used as a reliable indicator of Mid-Pliocene $\delta^{18}{\rm O}_{\rm sw}$ and sea level, and in turn can provide estimates of variability in Mid-Pliocene continental ice volume. If so, the results presented here would be consistent with significant fluctuations in continental ice volume

during the Mid-Pliocene warm period. The largest continuous shifts in $\delta^{18}O_{sw}$, ice volume and sea level during the Mid-Pliocene occurred during cooling events at the MG1/M2, KM3/KM2 and G17/G16 transitions, each displaying a sea level decrease of 65 m or more. For most of the Mid-Pliocene warm period, sea level fluctuated within a range of approximately 25 m above and 25 m below modern sea level. This approximately 50 m range represents roughly 42 per cent of the typical 120 m range for the Late Quaternary glacial—interglacial cycles.

These data provide reasonable estimates of the total changes in continental ice volume, but not direct evidence for the location of Pliocene land-based ice. Assuming roughly similar atmospheric and oceanic circulation between modern and Mid-Pliocene, the data imply significant build-up of continental ice volume, including in the Northern Hemisphere, during the extreme low-stand events at M2, KM2, G20 and G16. Similarly, the extreme high-stand events at KM5, KM3, K1 and G17 indicate significant melting of Antarctic continental ice, perhaps as much as 25–30 per cent.

4. Summary and conclusions

We combined ostracode Mg/Ca-based BWTs with benthic foraminiferal oxygen isotopes at DSDP Site 607 in the North Atlantic in order to quantify the oxygen isotopic composition of seawater, and in turn provide estimates of the extent of continental ice volume and sea-level variability during the Mid-Pliocene warm period (ca 3.3-3.0 Ma). We applied a new technique that includes a straightforward water-mass normalization factor that improves considerably upon earlier applications of the Mg/Ca–BWT–benthic δ¹⁸O approach. Validity tests on Late Quaternary Mg/Ca and benthic δ¹⁸O data from Site 607 and on Mid-Pliocene data from two additional North Atlantic sites suggest that the approach provides reliable estimates of Mid-Pliocene sea level and ice volume. Results indicate that following a low stand of approximately 65 m below present at MIS M2 ca 3.3 Ma, sea level generally fluctuated by 20–30 m above and below a mean value similar to present-day sea level. In addition to the low-stand event at MIS M2, significant low stands occurred at MIS KM2 (-40 m), G22 (-40 m) and G16 (-60 m), probably representing significant build-up of Northern Hemisphere ice sheets. Six high stands of +10 m or more above present day were also observed; four events (+10, +25, +15 and +30 m) from MIS M1 to KM3, a high stand of +15 m at MIS K1, and finally a high stand of +25 m at MIS G17. These results indicate that continental ice volume varied significantly during the Mid-Pliocene warm period, including times of reduced Antarctic ice volume. Correlation of the sea-level history derived here to sea-level records from continental shelf sequences is beyond the scope of this paper but should be evaluated in future investigations as a further test of the validity of the BWTbenthic δ^{18} O approach.

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